Emulsion Stabilization by Particles and Amphiphilic Polymers for Oil Spill Remediation

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**Background and Motivation**

Marine oil spills cause detrimental effects on ecosystems due to the spreading of oil on the ocean surface. One way to combat oil spills is by utilizing dispersants, which reduce the oil-water interfacial tension, allowing for oil droplet formation and dilution through the water column, thus accelerating the degradation process by bacteria and solar energy. Even though current dispersants are relatively non-toxic, they still add solvents and contaminants to the environment due to the large amounts used. In this work, we use the example of mineral particles in dispersants in order to reduce the amount of surfactants utilized and to develop formulations that have low impact on the environment.

**Dispersants Components:** surfactants, solvents, various additives

Over 2 million gallons used in the BP Deepwater Horizon oil spill!

**Advantages:**
- Use over a wide range of sea conditions
- Enhances the process of natural dispersion
- New dispersants are relatively non-toxic
- Reduce the oil tendency to stick to surfaces

**Disadvantages:**
- Limited time window (a couple of days)
- Loss effectiveness with time
- Not effective for all oil types (heavy oils disperse poorly)
- Requires some minimum amount of energy

**Objectives:**
- Investigate the interactions between particles and surfactants at oil-water interfaces
- Obtain a fundamental understanding of wetting and adhesion of oil on silica, or oil removal from surfaces.
- Investigate the mechanism of Oil-Mineral Aggregates (OMAs) formation.
- Design effective and environment-friendly dispersants containing less or no surfactants.

**Materials and Methods**

**Oil/Water Components:**
- Hexadecane and toluene

**Surfactant:**
- Pluronic F127 (PEO<sub>20</sub>PO<sub>7</sub>PEO<sub>20</sub>)
- POP block is hydrophobic, PEO is hydrophilic

**Particles:**
- Silica (SiO<sub>2</sub> LUDOX TM 50, 26nm)

**Emulsion Preparation**
- Oil-water (20/80 v/v) mixtures were homogenized by IKA Ultra Turrax T-25 Homogenizer in 10 mL vials.
- Mixing energy: IKA Ultra Turrax T-25 Homogenizer 13k rpm, 5min.

**Emulsion Evaluation**
- Emulsion stability was determined by measuring the volume fractions of oil, emulsion and aqueous phases over time.
- Oil droplet sizes were determined by optical microscopy.

**Effect of Silica Particles on Emulsion Stability**

Silica particles alone do not stabilize the emulsions, neither in hexadecane-water system nor in toluene-water system.

**Effect of Surfactants on Emulsion Stability**

**Oil, water, and emulsion fractions**

**Hexadecane-water system**
- F127 concentrations below 0.003 wt% do not produce stable emulsions
- P127 concentrations above 0.005 wt% produce stable emulsions

**Toluene-water system**
- F127 concentrations below 0.003 wt% do not produce stable emulsions
- P127 concentrations above 0.005 wt% produce stable emulsions

**Droplet sizes and distributions**

**Hexadecane-water-surfactant-particle system after 3 hours**
- Emulsion with particles demonstrate a more narrow droplet size distribution
- 0.01 wt% silica content showed more resistance toward creaming, this is due to the presence of higher amounts of smaller droplets
- Small droplets rise more slowly due to decreased buoyant forces and are responsible for better creaming stability
- Emulsions with 0.25 wt% silica show larger droplet sizes and hence lower creaming stability

**Synergistic Effects**

Hexadecane-water based emulsions

- At lower concentrations (0.001 wt%), F127 can prevent the droplet coalescence resulting in lower emulsion stability
- Synergistic interactions exist between silica particles (1 wt%) and F127 (0.001 wt%) preventing droplet coalescence and contributing to enhanced emulsion stability

**Regions of increased stability to creaming identified:**
- Hexadecane-F127(0.005 wt%)-Silica(0.1 wt%)
- Toluene-F127(0.005 wt%)-Silica(0.05-0.1 wt%)

**Summary**

- Silica particles alone were not able to stabilize the emulsions
- F127 at concentrations below the critical micellization concentration (CMC), localizes at the oil-water interface, creating stable emulsions
- Synergistic interactions between particles and polymers contribute to enhanced stability of the emulsions

**References**

- Bull. 79, 16
- Molecular Engineering of Oil-Mineral Aggregates (OMAs) formation under various conditions: 1. Mineral type, size and concentration 2. Dispersant characteristics 3. Oil type and concentration 4. Solubility, temperature, pressure, and dilution conditions

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**Tables:**

- Oil, water, and emulsion fractions
- Droplet sizes and distributions

**Figures:**

- Emulsion types
- Effect of Surfactants and Particles on Emulsion Stability
- Synergistic Effects

**Images:**

- Emulsion stabilization by particles and amphiphilic polymers for oil spill remediation
- Diagrams showing emulsion and droplet fractions at different times

**Graphs:**

- Graphs illustrating the concentration of F127 (weight %) versus oil fraction, emulsion fraction, and aqueous fraction at different times (1 hour, 1 day, 3 hours).

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